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Charge Transfer Complexes. Competition between Donor and Solvent for the Acceptor. A New Method of Study. Case of Maleic Anhydride and Vinyl Monomers: Styrene and Vinyl Acetate

Claude Caze^a; Claude Loucheux^a

^a Laboratoire de chimie macromoléculaire, Université des Sciences et Techniques de Lille, Villeneuve d'Ascq, France

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**Charge Transfer Complexes. Competition
between Donor and Solvent for the Acceptor.
A New Method of Study. I. Case of Maleic
Anhydride and Vinyl Monomers:
Styrene and Vinyl Acetate**

CLAUDE CAZE and CLAUDE LOUCHEUX

Laboratoire de chimie macromoléculaire
Université des Sciences et Techniques de Lille
59 650 Villeneuve d'Ascq, France

ABSTRACT

Charge transfer complexes between maleic anhydride and vinyl monomers have been investigated by using UV absorption techniques. A short review of the application of this technique to our problem has been made. Starting from the assumptions assumed by Merrefield and co-workers, we have developed a new method of taking account of the possibility of complexation between the acceptor and the solvent.

INTRODUCTION

Charge transfer complexes exhibited by maleic anhydride have been extensively investigated (e.g., Refs. 1-3). However, the problem of the influence of the solvent is not yet completely

elucidated. Starting from the Benessi-Hildebrand technique [4], we propose a new method of investigation taking into account the possibility of complexation of maleic anhydride with the solvent. The maleic anhydride-styrene system has been used for testing the method. Then the vinyl acetate-maleic anhydride system has been studied.

THEORY

In solution, when a charge transfer complex (CT) between an electron donor (ED) and an electron acceptor (EA) is obtained, we have an equilibrium:



The constant K of this equilibrium is defined as

$$K = \frac{[\text{CT}]}{[\text{ED}][\text{EA}]} \quad (1)$$

Where $[\text{CT}]$, $[\text{ED}]$, and $[\text{EA}]$ are the concentrations of the species CT, ED, and EA, respectively. The UV absorption technique is very often used for the determination of K .

Classical Methods of Measuring K

In the Benessi-Hildebrand technique, absorption measurements at a wavelength λ , where ED and EA do not absorb, provide the optical density d_λ of the complex:

$$d_\lambda = \epsilon_{\text{CT},\lambda} l [\text{CT}] \quad (2)$$

$\epsilon_{\text{CT},\lambda}$ is the molar extinction coefficient of the charge transfer complex, and l is the length of the optical path in the measurement cell.

If we assume the condition

$$[ED] \gg [EA], \text{ i.e., } [ED] = \text{constant}$$

and if $[EA]_0$ is the initial concentration of the electron acceptor, the following relationship can be written:

$$\frac{l[EA]_0}{d_\lambda} = \frac{1}{\epsilon_{CT,\lambda}} - \frac{1}{\epsilon_{CT,\lambda}} \frac{1}{K} \frac{1}{[ED]} \quad (3)$$

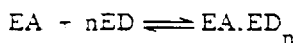
In a set of experiments where $[ED]$ and $[EA]_0$ are known, plotting $l[EA]_0/d_\lambda$ against $1/[ED]$ permits the determination of $\epsilon_{CT,\lambda}$ and K .

Other methods have been proposed by many authors for measuring K . Scott [5] uses the Benesi-Hildebrand equation in the form:

$$\frac{l[EA]_0[ED]}{d_\lambda} = \frac{1}{K} \frac{1}{\epsilon_{CT,\lambda}} + \frac{[ED]}{\epsilon_{CT,\lambda}} \quad (4)$$

Plotting $l[EA]_0[ED]/d_\lambda$ against $[ED]$ yields more precise values of $\epsilon_{CT,\lambda}$ and K .

Foster, Hammick, and Wardley [6] gave a generalization of the Benesi-Hildebrand method when the stoichiometry of the complex is different from 1, 1. The preceding equilibrium becomes



If $[CT]$ is the concentration of the $EA \cdot ED_n$ complex, K is defined as

$$K = \frac{[CT]}{[EA][ED]^n} \quad (5)$$

If we assume $[ED] \gg [EA]$, and if the measured optical density d_λ of the solution is

$$d_\lambda = \epsilon_{CT,\lambda} l[CT]$$

we obtained the new relation

$$K\epsilon_{CT,\lambda}[EA]_0 - Kd_\lambda = d_\lambda [ED]^n \quad (6)$$

The determination of the association degree n of the complex is made by plotting $d_\lambda [ED]^n$ against d_λ for different values of n .

When a straight line is obtained, n and K are deduced simultaneously.

Drago and Rose [7] discussed the approximation that the complex concentration is negligible with respect to the concentration $[ED]$ of the electron donor, and then calculate the constant K .

Several authors have remarked that in certain cases the Benessi-Hildebrand method gives zero for the interception value $1/\epsilon_{CT,\lambda}$ which corresponds to an infinite value of $\epsilon_{CT,\lambda}$. Person [8] showed that the Benessi-Hildebrand method gives such a zero interception if the concentration ratio $[ED]/[EA]$ does not verify the relation

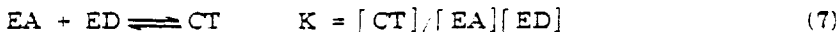
$$10\%[EA]_0 < [CT] < 90\%[EA]_0$$

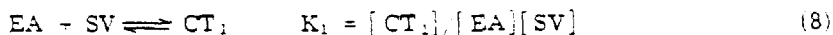
Hammond [9] showed that the accuracy of the Benessi-Hildebrand method is very weak when K is small. For values of K lower than 0.1, the uncertainty of the result is of the same order of magnitude as the result itself.

Orgel and Mulliken [10] interpreted this particular case by assuming that the hypothesis of "contact charge transfer" exists simultaneously with the charge transfer complex in the solution. These "contact charge transfers" would not respect the mass-action law.

Carter, Murrell, and Rosch [11] criticized the Orgel-Mulliken assumption: 1) there is no thermodynamic justification for the hypothesis of the existence of such a "contact charge transfer"; 2) the part played by the solvent is not taken into account, and in the case of complexes with a low formation constant, a competition exists between the donor and the solvent to occupy the sites around the acceptor.

For this purpose, Merrefield and Phillips [12] postulated competition between donor and solvent around the acceptor sites. If SV is the solvent, then





If $d_\lambda = \epsilon_{CT,\lambda} l [CT]$, then

$$\frac{[EA]_0 l}{d_\lambda} = \left(\frac{1 - K_1}{K \epsilon_{CT,\lambda}} \right) \frac{1}{[ED]} - \frac{1}{\epsilon_{CT,\lambda}} \left(1 - \frac{K_1}{K} \right) \quad (9)$$

The corresponding plot provides essentially K_1 , K .

New Method Proposed for Measuring K

The classical methods reviewed are not available in the case where there is competition between the solvent and the electron donor around the acceptor sites. From Eqs. (7) and (8), that is, when assuming the formation of two 1:1 complexes, and with the supplementary conditions $[ED] \gg [EA]$ and $[SV] \gg [EA]$, we can write

$$[ED] = \text{constant and } [SV] = \text{constant.}$$

We have the concentration relation

$$[EA]_0 = [EA] + [CT] + [CT_1]$$

At a wavelength λ , where $\epsilon_{CT,\lambda}$ and $\epsilon_{EA,\lambda}$ are the molar extinction coefficients for the charge complex transfer CT and for the acceptor EA, respectively, the optical density d_λ measured is

$$d_\lambda = \epsilon_{CT,\lambda} l [CT] + \epsilon_{EA,\lambda} l [EA]$$

Then

$$\frac{d_\lambda}{l [EA]_0} = \frac{\epsilon_{CT,\lambda} K [ED] + \bar{\epsilon}_\lambda (1 - K_1 [SV])}{1 + K [ED] + K_1 [SV]} \quad (10)$$

where $\bar{\epsilon}_\lambda$ is the apparent molar extinction coefficient of the acceptor in the solvent SV at the wavelength λ . $\bar{\epsilon}_\lambda$ is obtained from the slope of the straight line $d_\lambda = f([EA]_0)$.

If there exists between the concentrations $[SV]$ and $[ED]$ a linear relation such as

$$[SV] = a - b[ED] \quad (11)$$

Then Eq. (10) becomes

$$\frac{d_\lambda}{l[EA]_0} = \frac{\bar{\epsilon}_\lambda(1 + K_1a) + [ED](\epsilon_{CT,\lambda}K - \bar{\epsilon}_\lambda K_1b)}{1 - K_1a + [ED](K - bK_1)} \quad (12)$$

$\bar{\epsilon}_\lambda$ is determined by preliminary experiments. If a constant volume of solution is used, a and b are known. In these conditions, K , ϵ_{CT} , and K_1 are calculated by the least squares method applied to the function $d_\lambda/l[EA]_0 = f([ED])$.

RESULTS

Maleic Anhydride-Styrene System

This system has been studied in two solvents of very different dielectric constants: chloroform ($\epsilon = 4.3$ at 20°C) and acetone ($\epsilon = 20.7$ at 25°C). The optical density values have been determined with a Beckman DBG spectrophotometer equipped with a T_M analyzer which allows the temperature to be programmed between 0 and 100°C .

Measurements in Chloroform

We have studied the charge transfer band of the complex at 340 and 345 nm. For these wavelength values there is a weak absorption of maleic anhydride at the concentrations used. The optical density d_λ is

$$d_\lambda = \epsilon_{CT,\lambda}l[CT] - \epsilon_{MA,\lambda}l[MA] \quad (13)$$

where $[MA]$ and $\epsilon_{MA,\lambda}$ are the molar concentration of maleic anhydride and the corresponding extinction coefficient, respectively.

In this case the Benesi-Hildebrand method may be applied by taking into account the relation [13]

$$\frac{l[MA]_0}{d_\lambda^*} = \frac{1}{\epsilon_{CT,\lambda} - \epsilon_{MA,\lambda}} - \frac{1}{\epsilon_{CT,\lambda} - \epsilon_{MA,\lambda}} \frac{1}{K} \frac{1}{[ST]} \quad (14)$$

where $[ST]$ is the styrene molar concentration, $[MA]_0$ is the initial molar concentration of maleic anhydride, and

$$d_\lambda^* = d_\lambda - \epsilon_{MA,\lambda} l [MA]_0$$

Figure 1 represents the variation of $l[MA]_0/d_\lambda^*$ vs $1/[ST]$.

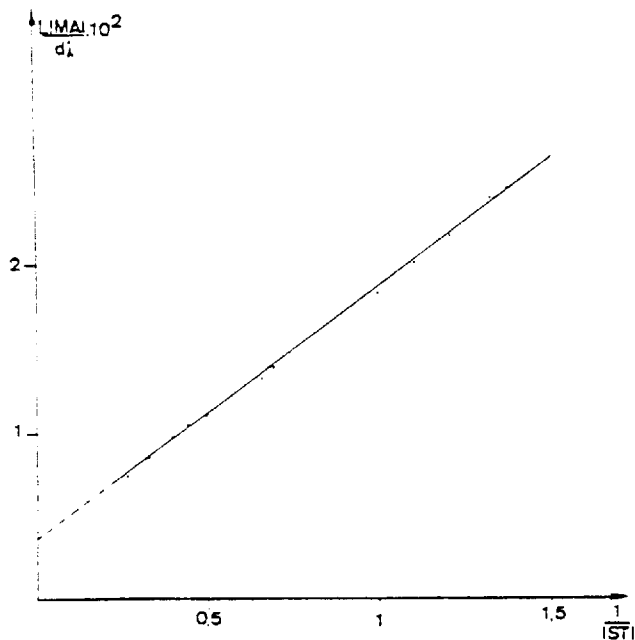


FIG. 1. Maleic anhydride-styrene system in chloroform. Temperature = 25°C. $\lambda = 340$ nm.

Figure 2 is a plot of the variation of d_{λ} (Eq. 13) vs the styrene concentration. The experimental conditions were

$$[\text{MA}]_0 = 0.5 \times 10^{-2} \text{ mole/liter}$$

and $0.72 \text{ mole/liter} < [\text{ST}] < 3.75 \text{ mole/liter}$.

The values of K have been determined both by using the Benesi-Hildebrand method and by our new method. The value of K_1 has been obtained by our new method. Table 1 summarizes the results.

From Table 1 we see that the constant K_1 of complexation between maleic anhydride and chloroform is zero. The charge

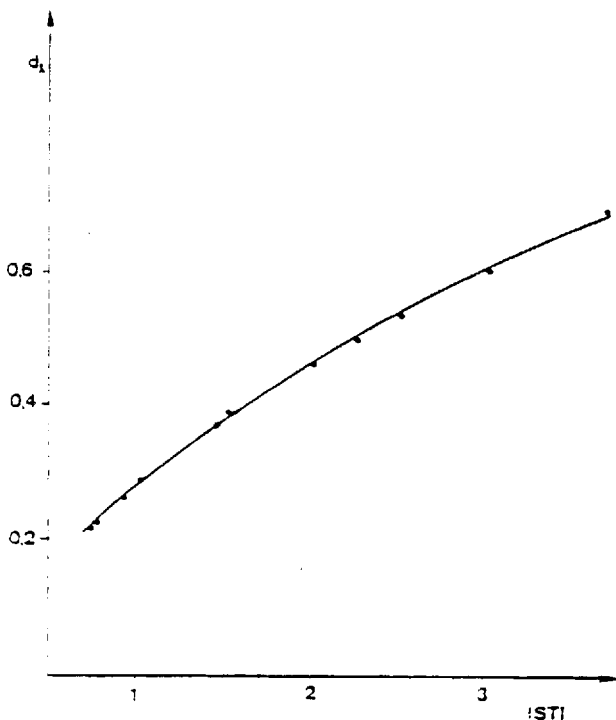


FIG. 2. Maleic anhydride-styrene system in chloroform. Optical density against styrene concentration. Temperature = 25°C. $\lambda = 340 \text{ nm}$.

TABLE 1. Maleic Anhydride-Styrene System

λ (nm)	Benessi-Hildebrand method		Our method		
	$\epsilon_{CT,\lambda}$	K (liter/mole)	$\epsilon_{CT,\lambda}$	K (liter/mole)	K_1 (liter/mole)
340	294	0.24	287	0.27	0.00
345	220	0.24	180	0.28	0.00

transfer complex constant K between styrene and maleic anhydride obtained is the same whatever the method used. The accuracy of the values of K is approximately 10%.

The variation of K with temperature has been followed. The values of K have been calculated by the Benessi-Hildebrand method. Figure 3 represents the variation of $\ln K$ vs $1/T$. A linear plot is obtained from which the variation of enthalpy ΔH for the formation of the complex is deduced as $\Delta H = -2.5 = 0.35$ kcal/mole.

Measurements in Acetone

The experimental conditions were $[MA]_0 = 10^{-2}$ mole/liter; 1.5 mole/liter $< [ST] < 7.2$ mole/liter; and $\lambda = 340$ and 345 nm. The temperature was 25°C, $a = 13.64$ and $b = 1.564$.

Figure 4 represents $d_\lambda = f([ST])$. Figure 5 represents $f([MA]_0, d_\lambda^* = f(1/[ST]))$, using the Benessi-Hildebrand method.

It may be seen that the intercept of the curve gives a negative value. Because acetone is an electron donor, a maleic anhydride-acetone complex may be formed.

By applying our method to this system, the results of Table 2 are obtained.

TABLE 2. Maleic Anhydride-Styrene System. Our Method

λ (nm)	$\epsilon_{CT,\lambda}$	K (liter/mole)	K_1 (liter/mole)
340	554	0.20	0.79
345	367	0.21	0.75

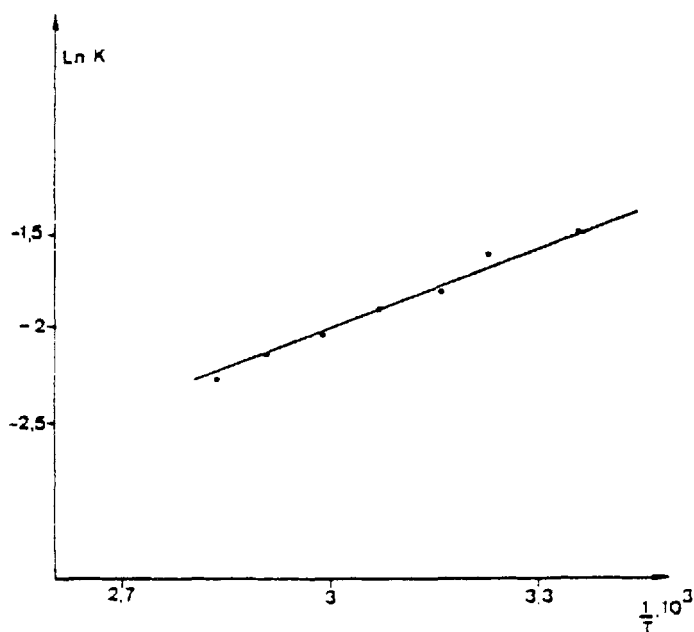


FIG. 3. Maleic anhydride-styrene system in chloroform. Arrhenius plot of the constant K .

The values of the K_1 constant in Table 2 show that in this system the complexation of maleic anhydride with the solvent acetone is the main phenomenon.

Maleic Anhydride-Vinyl Acetate System

The study of this system has been performed only in chloroform because of the low values of the constant K for this pair of monomers. The results have been interpreted by using Relation (14), the concentration of vinyl acetate $[VA]$ being substituted for the concentration of styrene $[ST]$.

The experimental conditions were $[MA]_0 = 10^{-2}$ mole/liter and 3 mole/liter $< [VA] < 6$ mole/liter. The temperature was 25°C, and $\lambda = 280$ and 275 nm. Table 3 gives the results.

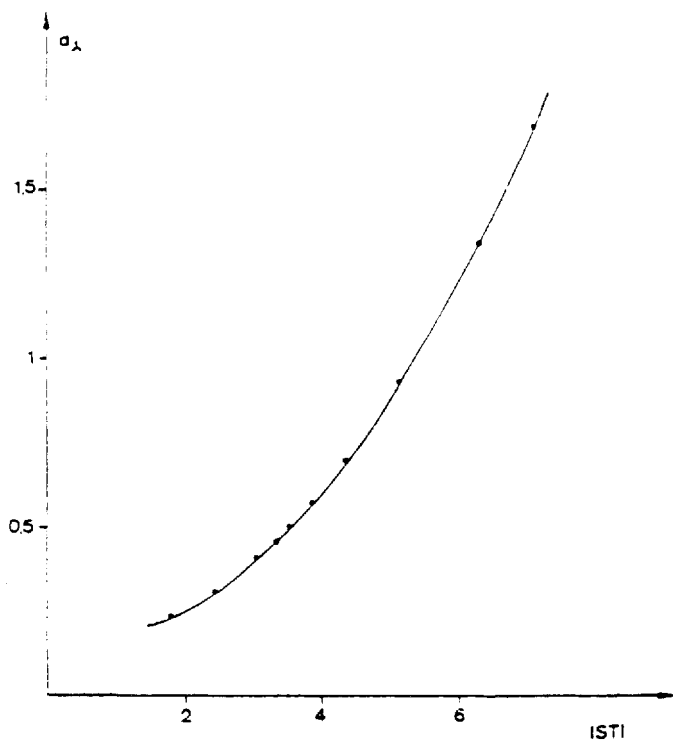


FIG. 4. Maleic anhydride-styrene system in acetone. Optical density against styrene concentration. Temperature = 25°C. $\lambda = 340$ nm.

TABLE 3. Maleic Anhydride-Vinyl Acetate System. Benesi-Hildebrand Method

λ (nm)	$\epsilon_{CT,\lambda}$	K (liter/mole)
280	150	0.066
275	217	0.063

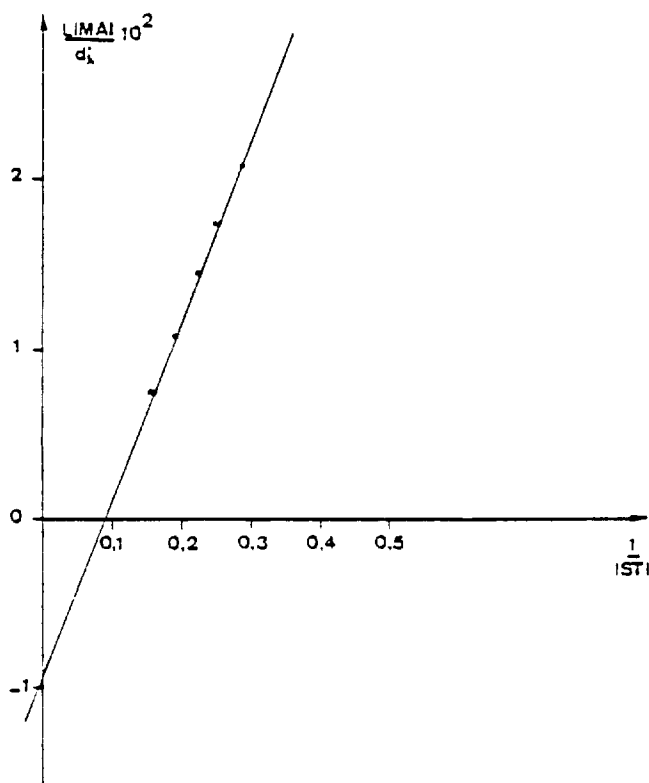


FIG. 5. Maleic anhydride-styrene system in acetone. Temperature = 25°C. $\lambda = 340$ nm.

DISCUSSION

The values of the constants we have determined may be compared with those given in the literature. In the case of the maleic anhydride-vinyl acetate system, we have found no result to compare with ours. Matsuda and Abe [2] have measured the constant K for the maleic anhydride-styrene system in chloroform at room temperature and find $K = 0.05$ liter/mole. This value is much lower than $K = 0.27$, given in Table 1. Tsuchida, Tomono, and Sano [13] have studied the formation of the complex in different solvents by using NMR techniques. They ascribe the low value

TABLE 4. Comparison of Our Results with Those of Tsuchida et al.

AM (mole/liter)	ST (mole/liter)	Acetone (mole/liter)	Our results			Tsuchida et al.		
			$CT \times 10^3$ (mole/liter)	$CT_1 \times 10^2$ (mole/liter)	$CT \times 10^3$ (mole/liter)	$CT \times 10^2$ (mole/liter)	$CT_1 \times 10^3$ (mole/liter)	$CT_1 \times 10^2$ (mole/liter)
0.40	1.60	10.73	12.9	34.1	12.4	33.5		
0.70	1.30	10.94	18	59.7	16.8	59.3		
1.00	1.00	11.13	19.5	85.7	17.7	85.6		
1.30	0.70	11.34	17.5	113.1	15.4	112.5		
1.60	0.40	11.54	12.1	140.9	10.3	139.7		

found by Matsuda and Abe to a complexation of maleic anhydride with chloroform. According to the results of Table 1, we see that this kind of complex does not exist. We can compare our results in acetone to those obtained by Tsuchida and co-workers; here the agreement is quite good and confirm that in this solvent the formation of a maleic anhydride-acetone complex prevails.

Table 4 compares our results with those of Tsuchida.

The Merreffield and Phillips method applied to the maleic anhydride-styrene system in acetone gave no results.

CONCLUSION

When there is no possibility of a complexation between the solvent and one of the two components of a complex, the Benessi-Hildebrand technique can be applied successfully. If such a complex does exist, our new method of investigating permits the calculation of the two formation constants K and K_1 . The example of the maleic anhydride-styrene system is very convincing, our results being in good agreement with those obtained under the same conditions by NMR techniques.

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